Electrochemical Nanostructuring

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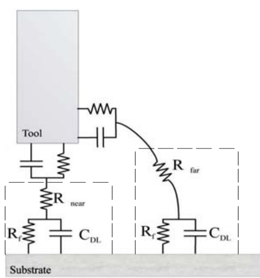
Abstract

An electrochemical method suitable for the fabrication of micro- and nanostructures on conducting and semiconducting substrates is electrochemical machining with ultrashort voltage pulses. This technique has been utilized to create nanostructures with features approaching 100 nm on metallic and p-Si substrates. The electrochemical machining of the nanostructures on p-Si substrates generates a localized defect structure that is successively utilized to achieve selective metallization of the nanostructures. Electrochemical machining with ultrashort voltage pulses is also used as the first step in a micro-contact printing procedure to fabricate the master for a polymer stamp to be used in the printing process.

Fundamentals of Electrochemical Machining with Ultrashort Voltage Pulses

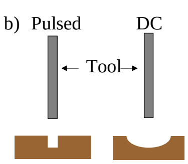
Micro- and nanofabrication is accomplished electrochemically through the application of ultrashort voltage pulses to a micro- or nanoscale tool electrode. The tool electrode is used to machine its inverse on a suitable metallic or p-Si substrate electrode. The ultrashort pulses are necessary because current does not only take the shortest route from the tool electrode to the substrate electrode; it also spreads throughout the electrolyte. The ultrashort pulses preserve the resolution of the tool electrode by taking advantage of the capacitor-like behavior of the electrochemical double layer surrounding the substrate electrode and the inverse relation between the distance of a current path from the tool electrode to the substrate electrode and the resistance of a current path.

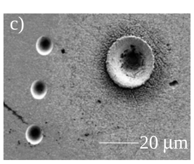
a)



a) This schematic illustrates the circuit analog of two possible current paths from the tool electrode to the substrate electrode. The current path designated by R_{far} can effectively be negated through the use of ultrashort voltage pulses allowing for enhanced resolution versus DC.

b)

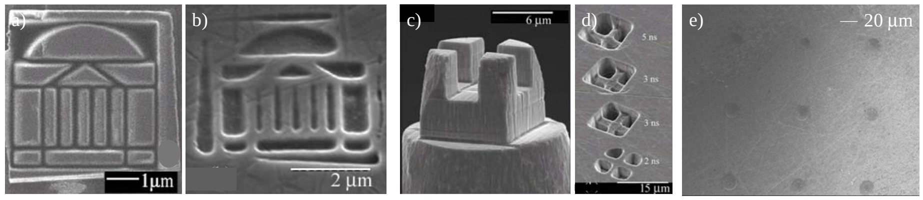




b) Illustration of ultrashort voltage pulse versus DC machining.

c) Cu substrate machined with ultrashort voltage pulses (left) and DC (right).

Metallic Machining



a) W tool electrode of the UVa rotunda fabricated with a Focused Ion Beam (FIB).

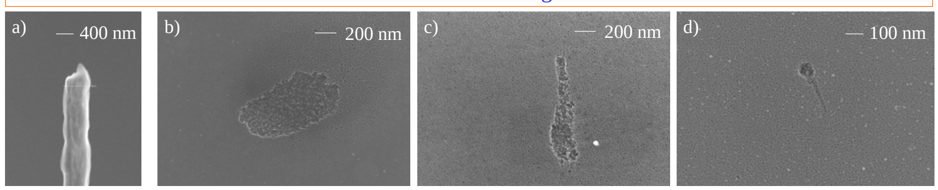
b) UVa rotunda machined with 2 ns pulses into a Ni substrate to a depth of 400 nm. The inner columns of the rotunda are approximately 120 nm in width.

c) Four prong W tool electrode fabricated with a FIB.

d) The tool from c) is used to machine a Ni substrate to demonstrate the improvement in resolution that occurs with shorter pulse durations.

e) 3 x 3 array machined with 10 ns pulses into a Cu substrate. Each circular feature is 15 µm in diameter and 6 µm in depth.

Silicon Machining



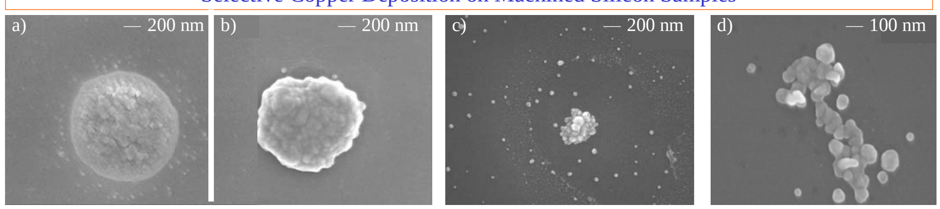
a) A typical W tool electrode used in the machining of p-Si.

b) A nanoscale feature with a width of 700 nm machined with 50 ns pulses into a p-Si substrate. The p-Si experiments were done with B-doped 0.001-0.002 Ω•cm p-Si substrates in a 1 M HF electrolyte and machined to an approximate depth of 300-500 nm.

c) A rectangular feature 200 nm in width and 1 µm in length machined with 50 ns pulses into p-Si.

d) A circular feature 100 nm in diameter machined with 40 ns pulses into p-Si.

Selective Copper Deposition on Machined Silicon Samples



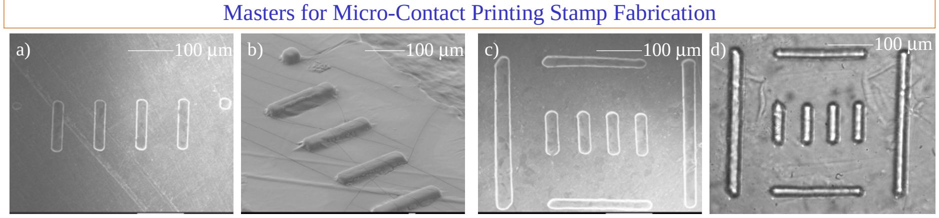
a) A circular feature 1 µm in diameter machined with 30 ns pulses into p-Si before DC Cu deposition.

b) The p-Si substrate from a) after DC Cu deposition. The deposition experiments were performed using a double pulse technique in a $CuSO_4$ + H_2SO_4 electrolyte.

c) A selective nanoscale Cu deposit on p-Si machined with 30 ns pulses.

d) Another example of a selective nanoscale Cu deposit on p-Si machined with 30 ns pulses.

Masters for Micro-Contact Printing Stamp Fabrication



a) Ni master machined with 30 ns pulses with features 15 µm in width, 100 µm in length, and 10 µm in depth.

b) Polydimethyl siloxane (PDMS) stamp fabricated from the Ni master in a).

c) Ni master machined with 30 ns pulses with inner features 15 µm width, 60 µm in length, and 10 µm in depth. The outer features are 320 µm in length (vertical) and 240 µm in length (horizontal).

d) PDMS stamp fabricated from Ni master in c).

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Conclusions

Electrochemical machining with ultrashort voltage pulses is a viable technique for the fabrication of micro- and nanoscale features on metallic and p-Si substrates. The electrochemical machining of nanostructures on p-Si substrates provides sites for selective metallization. Metallic substrates machined with ultrashort voltage pulses can be utilized as the master for a polymer stamp to be used in a micro-contact printing procedure.

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